

**IZMIR KATIP CELEBI UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE AND  
ENGINEERING**

**NANOCELLULOSE-POLYPROPYLENE COMPOSITES**

**M.Sc. THESIS**

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**Department of Material Science and Engineering**

**Thesis Advisor: Assoc. Prof. M. Özgür SEYDİBEYOĞLU**

**NOVEMBER 2015**

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**İZMİR KATİP ÇELEBİ ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ**

**NANOSELÜLOZ-POLİPROPİLEN KOMPOZİTLERİ**

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**Malzeme Bilimi ve Mühendisliği Anabilim Dalı**

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**Date of Submission: 12 November 2015**  
**Date of Defense : 13 November 2015**

*To my family,*

## ACKNOWLEDGEMENT

I would especially like to thank my advisor, Assoc. Prof. Mehmet Özgür Seydibeyođlu, for his healthy degree of optimisms. He answered all my questions in detail with patience and he never hesitated to spend his valuable time to help me.

Next, I would like to thank my group members who encouraged me to continue to work hard when motivation was low, provided advice when I was stumped and lost, delivered comic relief when it was sorely needed and reminded me the important things in life when I forgot. I would also like to thank my lab mates Tuđçe Uysalman, Hilal Kara, Metehan Atagür.

Next, I would like to thank my friends Abdullah Bayram, Cebrail Özbek, Emre Arkan and Hande Alptekin for their support, kindness and friendship.

This Thesis was supported by the project of SANTEZ. This project was carried out by İzmir Katip Çelebi University, Ministry of Science, Industry and Technology and Farplas company.

Without great friends and family, this endeavor would have concluded before it began. I would like to thank them for believing in me, encouraging me to continue going, and providing distractions from work when they were needed.

I want to thank my parents. It is with their help for all my life that I became who I am today. Thanks for always being there for me, believing in me and motivating me to set out on my own path. I cannot begin to describe how lucky I feel for having them as my parents. All opportunities and accomplishments I owe to them.

November 2015

Ece YAKKAN

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## ABBREVIATIONS

<b>CO<sub>2</sub></b>	: Carbon dioxide
<b>GF</b>	: Glass Fibers
<b>PAN</b>	: Polyacrylonitrile
<b>WPCs</b>	: Wood–Plastic Composites
<b>PLA</b>	: Poly (lactic acid)
<b>PP</b>	: Polypropylene
<b>CNTs</b>	: Carbon Nano Tubes
<b>PVA</b>	: Polyvinyl Alcohol
<b>NFCs</b>	: Natural Fiber Composites
<b>CNF</b>	: Cellulose Nanofibers
<b>NC</b>	: Nanocellulose
<b>MAPP</b>	: Maleic Anhydride grafted Polypropylene
<b>Fusabond</b>	: Anhydride modified high-density polyethylene
<b>FTIR</b>	: Fourier Transform Infrared Spectroscopy
<b>TGA</b>	: Thermo Gravimetric Analysis
<b>DMA</b>	: Dynamic Mechanical Analysis
<b>CA</b>	: Contact Angle
<b>SEM</b>	: Scanning Electron Microscopy



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## NANOCELLULOSE-POLYPROPYLENE COMPOSITES

### SUMMARY

Material selection plays critical role not only for human life but also for engineering design of a successful sustainable product. Especially, importance of eco-friendly materials increases nowadays. In this regard, the importance of natural fiber reinforced composites is growing rapidly both in terms of their industrial application areas and unique properties. Natural fibers availability, renewability, low density and price as well as satisfactory mechanical properties make them an attractive ecological alternative to glass, carbon and other man-made fibers used for the manufacturing of composites

In this study, nanocellulose–polypropylene composites were manufactured via twin-screw extrusion technique with and without coupling agents. This study has three parts. In the first and most comprehensive part, nanocellulose–polypropylene composite containing 2wt % nanocellulose was manufactured. In the second part, nanocellulose–polypropylene composite was reinforced with the two different coupling agents such as MAPP and Fusabond. In the last step, composite materials were characterized in terms of their mechanical, thermal, spectroscopic, and morphological properties. The spectroscopic characterizations of the composites were performed to confirm the interfacial adhesion of polypropylene and nanocellulose. Furthermore, thermal behaviors and hydrophobicity of composites were studied by thermogravimetric analysis technique and contact angle measurements, respectively. The morphology of the composite was investigated via scanning electron microscopy (SEM). Finally, tensile test and dynamic mechanic analysis were conducted to determine the mechanical properties of materials.

The results showed a 38% increase in the tensile strength and showed an 87% increase in the Young's Modulus of nanocellulose–polypropylene composite containing coupling agent compared to that of neat polypropylene. Furthermore, the thermal stability of composite samples did not change much but slightly increase with addition of coupling agents. According to spectroscopic characterizations of the composite samples, the interfacial interaction between matrix and reinforcement phase was improved with addition of coupling agent. To conclude this comprehensive work on nanocellulose–polypropylene composites, it was observed that the properties of composite sample were improved with addition of coupling agent.

## NANOSELÜLOZ- POLİPROPİLEN KOMPOZİTLER

### ÖZET

Malzeme seçimi günlük yaşantımızda önemli bir role sahip olmasının yanısıra mühendislik uygulamalarda ve tasarımlarda ürün sürdürülebilirliği açısından da önemlidir. Özellikle, çevre dostu malzemelerin önemi günümüzde artmaktadır. Bu bağlamda, endüstriyel uygulama alanları ve eşsiz özelliklerinden ötürü doğal elyaf takviyeli kompozit malzemelerin önemi artmaktadır. Doğal elyafların kullanılabilirlik, yenilenebilirlik, düşük yoğunluk ve fiyata sahip olma gibi özelliklerinin yanı sıra tatmin edici mekanik özellikleri onları kompozit üretiminde kullanılan cam, karbon ve diğer insan yapımı elyafların çekici bir alternatifi yapmaktadır.

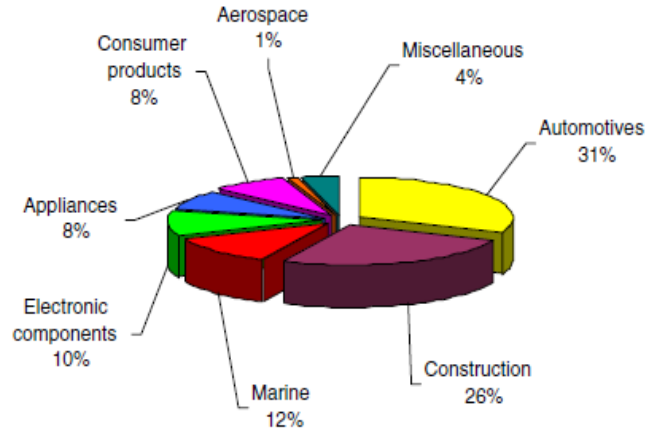
Bu çalışmada, nanoselüloz polipropilen kompozitleri çift vidalı ekstrüzyon tekniği ile birleştirme maddesi kullanılarak ve kullanılmadan üretilmiştir. Bu çalışma üç bölümden oluşmaktadır. İlk ve en kapsamlı bölümünde, ağırlıkça % 2 nanocellulose içeren nanocellulose-polipropilen kompozit üretilmiştir. İkinci bölümde, nanoselüloz-polipropilen kompozit iki farklı birleştirme maddesi ile takviye edilmiştir. Son bölümde, kompozit malzemeler mekanik, termal, spektroskopik ve morfolojik özellikleri bakımından karakterize edilmiştir. Kompozitlerin spektroskopik karakterizasyonu nanoselüloz ve polipropilenin arayüz etkileşimini göstermek için gerçekleştirilmiştir. Bundan başka, kompozitlerin termal davranışları ve hidrofobikliği, sırasıyla, termogravimetrik analiz tekniği ve temas açısı ölçümleri ile incelenmiştir. Kompozit morfolojisi taramalı elektron mikroskobu aracılığıyla araştırılmıştır. Son olarak, çekme testi ve dinamik mekanik analiz malzemelerin mekanik özelliklerini belirlemek amacıyla yapılmıştır.

Sonuçlar, saf polipropilen ile karşılaştırıldığında birleştirme maddesi içeren nanoselüloz ve polipropilenin kompozitinin mekanik dayanımının %38 ve elastik modül değerinin %87 oranında arttığını göstermiştir. Ayrıca, kompozitin termal kararlılığında önemli bir değişiklik olmamıştır fakat bağlama maddelerinin eklenmesi ile az miktarda artış göstermiştir. Kompozit örneklerin spektroskopik karakterizasyonlarına göre, matris ve takviye fazı arasındaki ara etkileşimi bağlama maddesinin eklenmesi ile geliştirilmiştir. Sonuç olarak, nanoselüloz-polipropilen kompozitleri ile gerçekleştirilen bu kapsamlı çalışmada kompozit numunenin özelliklerinin bağlama maddesinin eklenmesi ile geliştirilmiştir olduğu gözlemlenmiştir.

## 1. INTRODUCTION

In the past two decades, the concept of ‘eco-friendly material’ has gained significant importance because of the need to preserve our environment. The meaning of eco-friendly material contains ‘safe’ substance systems for human along with other life forms constantly. Material selection play critical role not only for human life but also, for engineering design of a successful sustainable product. Here, the most suitable concept for material selection is natural fiber reinforced composite materials. The importance of natural fiber reinforced composites is growing rapidly. Furthermore, these types of composite materials have some advantages such as availability, renewability, low density and price. In addition to these, fiber reinforced composites exhibits the good mechanical properties and all of these properties make them an attractive ecological alternative to carbon, glass, and other man-made fibers used for the manufacturing of composites [1, 2].

A broad definition of composite is that chemically distinct two or more materials combine to create a new material without lose their properties. The different types of materials can be combined to create a composite material without lose their properties. Therefore, composite materials have gained significant importance due to the increasing requirements for special materials. Within the developments in the technology, nanoscale and micron-sized reinforcements have become possible, which have many advantages in the field of materials and processing [3, 4]. Especially, new types of nanoscale reinforcements such as nanoclays [5], carbon nanomaterials [6], and nanocellulose [7] have a pioneering role in composite technology these new types of materials also exhibits the good mechanical and physical properties. Moreover, they have large number of application areas in automotive, constructions, marine, electronic, packaging [8] and aerospace [1, 9].



**Figure 1.1:** Wood plastic composites used in 2002 [9]

However, the major market identified for automotive industry. Especially, the natural fiber composite materials frequently apply as automotive components such as dashboards, door panels, parcel shelves, seat cushions, backrests, and cabin linings [10]. Audi, Opel, Daimler-Chrysler, Fiat, Ford, Mercedes Benz, Peugeot, Renault, Volvo, VW, Volkswagen, and BMW are known as important vehicle manufacturers and these manufacturers used the natural fiber reinforced composites in their vehicles in order to reduce the weight of automotive components [9, 10].

The other advantages of using natural fibers exhibit moderately high strength. Daimler Chrysler used the bast fibers due to greatest strength of the bast fibers. Furthermore, Daimler Chrysler reduced the weight of their products (between 10% and 30%) and also reduced the cost by using this fibers [9].

### **1.1. Polymeric Materials and Polymeric Composites**

Polymeric materials and composites are attractive for various applications because of many characteristics. These are low weight, low cost, ease of processing, and corrosion resistance. Polymeric composites consist of matrix phase and reinforcement [9]. The matrix phases consist of two major groups. These are known as thermosets and thermoplastics matrix materials [11]. The formulation of thermoset matrix is complex because these types of matrix materials consist of large number of components such as base resin, curing agents, catalysts, flowing agents, and hardeners [9]. Furthermore, these materials chemically cured at high temperature and they have highly cross-linked network structure. Compared to the thermoset polymers, thermoplastics offer many advantages.

The main advantage of thermoplastic matrix is their low processing costs. Another advantage is design flexibility and ease of molding complex parts [9]. Furthermore, simple methods such as extrusion and injection molding might be used for processing of these composites. Polyethylene [12-14], polypropylene [15, 16], polystyrene [17, 18], and poly(vinyl chloride) [19, 20] are known as the common types of thermoplastics and they commonly use in the industrial applications.

On the other hand, reinforcement materials use to improve chemical and/or physical properties of polymers. Reinforcement materials consist of two major groups. These are traditional reinforcements and natural reinforcements. Inorganic fibers (glass and carbon fibers) and aromatic organic fibers (Aramid) are known as traditional reinforcements in the polymers [21]. Natural fibers are subdivided based on their origins, coming from plants, animals or minerals. Although traditional fiber dominating the industrial applications, importance of natural fibers are growing day by day. Especially, natural fiber reinforced composites have been studied for decades as an important research area in the field of composite materials [9, 21]. Compare to the traditional fibers, natural fibers have some important advantages such as sustainability, renewability and lower costs. In addition to this, natural fibers offer environmental advantages such as reduced dependence on non-renewable energy/material sources, lower pollutant emissions, enhanced energy recovery and lower greenhouse gas emissions [22].

#### **1.1.1. Fiber reinforced polymer composites**

The main benefit of fiber loading of polymer matrix is providing stiffness, strength, thermal stability and other structural properties to the composites. The different types of fibers might be used as reinforcement for polymer composites but two groups of fibers are commonly use. These are traditional fibers and natural fibers. Glass, carbon and aramid fibers are used as traditional fibers and they are dominating in the industrial applications. Another important fiber type is natural fibers. These types of fibers have gained significant importance due to their properties such as sustainability, renewability and lower costs for composites materials [9, 22].

#### **1.1.2. Matrix Materials**

Plastics are categorized as thermoset or thermoplastic, based on their structure and their behavior. Thermoset and thermoplastic materials are defined as a matrix

material for polymer matrix composites. Composite materials might be considered as the most beneficial materials ever developed due to the large application areas. Especially, polymer matrix composites play important role in our lives because they can be designed as limitless objects such as vehicle components, bottles, and soft fabrics [11].

#### **1.1.2.1. Thermosets**

Thermosetting plastics consist of cross-linked or network structures and the molecules are bonded covalently between each other. Moreover, thermosetting plastics are prepared in two stages. In the first stage, long chain molecules, which are designed for further reaction collectively, are produced. In the second stage, heat is applied and some additives such as curing agents, catalysts, and hardeners are added in order to designing a complex cross-linked polymer bonded [23]. Furthermore, thermosetting plastics cannot be recycled and they commonly used in applications that demand high resistance to heat. Epoxy resins, unsaturated polyesters, alkyds, vinyl esters, phenolic, amino plastics, urethanes, silicones and furfural are known as important thermosetting resins [24].

#### **1.1.2.2. Thermoplastics**

Thermoplastic is a material based on polymer which can be shaped, in a viscous state at a temperature either higher than its glass transition temperature or higher than its melting temperature. If thermoplastic is shaped at a temperature higher than its glass transition temperature, it is defined as amorphous thermoplastics. If thermoplastic is shaped at a temperature higher than its melting temperature, it is defined as semi-crystalline thermoplastics. The process of melting and solidification are reversible for thermoplastics. Moreover, they can be reshaped in the case of heat and pressure application but some deteriorations are observed in the inside properties of thermoplastics in the each cycle producing. Compared to thermosets, thermoplastics generally require less time to solidify [25, 26]. Furthermore, thermoplastics are composed of long, linear or branched molecules but these molecules chemically separated from each other.

In contrast to thermosets, thermoplastics have many advantages. The main advantage of thermoplastic matrix composites is that their low processing costs and they can be manufactured by simple processing methods [27]. Important commercial examples



of thermoplastics include polyethylene [28], polyvinylchloride [29, 30], polystyrene [31], polypropylene [32], polyamides [33], polycarbonate [34], polyacetals [35, 36], and polyesters [25].

### **1.1.3. Types of Fibers**

#### **1.1.3.1. Traditional fibers**

Traditional fibers are composed of three major groups. These are glass fibers, carbon fibers, and aramid fibers. Glass fibers are defined as the most common types of reinforcement for polymer matrix composites. They are subdivided into three groups, which are E-glass, S-glass and C-glass. The main benefits of these fibers are their low cost, high tensile strength, and high chemical resistance.

In addition to these properties, they exhibit insulating properties. E-glass and S-glass fibers more commonly used as reinforcement in the plastic industry. E-glass fibers have the lowest cost. Therefore, they commonly used in the fiber-reinforced plastic industry. S-glass fibers have the highest tensile strength among all fibers in use. However, the manufacturing cost of S-glass fibers make it more expensive than E-glass [37, 38].

Another type of traditional fibers is carbon fibers. These fibers exhibit high-performance and they are most commonly used in civil engineering applications. Large varieties of fibers called precursors are used to produce carbon fibers of different morphologies and different specific characteristics. The most prevalent precursors are carbon fibers-rayon precursors, polyacrylonitrile (PAN) precursors, and pitch precursor. PAN precursors are the major precursors for commercial carbon fibers. Pitch precursors also have high carbon yield at lower cost. They have lower thermal expansion coefficients than both the glass and aramid fibers. Their disadvantages include inherent anisotropy (reduced radial strength), high energy requirements in their production as well as relatively high costs [38].

The aramid fibers have great fatigue and creep resistance. Although several commercial classes of aramid fibers exist, the most common, Kevlar are used in structural applications [39].

### 1.1.3.2. Natural fibers

Natural fibers are an important research area, which have been studied for decades, for industrial applications of composite materials [9]. These fibers are composed of plants, animals or minerals based on their origins, coming from. Animal fibers generally consist of proteins including collagen and keratin.

These fibers are composed of plants, animals or minerals based on their origins, coming from. In general, animal fibers are composed of silk and animal hair and they contain protein including collagen and keratin. These types of fibers can be extracted from animals and hairy mammals. Sheep's wool, cashmere, alpaca hair, horse hairs are known as typical examples of animal hairs. Silk fiber can be derived from dried saliva of bugs or insects during the preparation of cocoons. Silks commonly define as protein polymers that spun into fibers by some Lepidoptera larvae such as silkworms, spiders, scorpions, mites and flies [40].

The properties of composites might be improved by loading of natural fibers. The mechanical properties of some important fibers are shown in Table 1.1 [11].

**Table 1.1:** Mechanical properties of natural fibres

Name of fibres	Density (g/cm <sup>3</sup> )	Elongation at break (%)	Tensile strength (MPa)	Young's modulus	References
Cotton	1.5-1.8	7.0-8.0	287-597	5.5-12.6	[40]
Jute	1.3- 1.4	1.5-1.8	393-773	13-26.5	[41]
Flax	<b>1.50</b>	2.7-3.2	345-1035	<b>27.6</b>	[40]
Hemp	<b>1.14</b>	<b>1.6</b>	690	30-60	[40, 41]
Ramie	<b>1.50</b>	1.2-3.6	400-938	61.4-128	[40, 41]
Sisal	<b>1.45</b>	2.0-2.5	511-635	9.4-22	[40]

Plant based natural fibers consist of cellulose, hemicelluloses and lignin structures [40]. Hemicelluloses comprise several polysaccharides that remain related to cellulose. Lignin is a complex polymer composed of phenyl propane unit. These components of natural fibers exhibit the differences between species and may affect the intrinsic properties of composites [42]. Johan and Paul [43] modified cellulose fibers with polypropylene-maleic anhydride copolymer. They studied two different fiber contents, which are %10 and %40, with and without coupling agents. In another work, Ru Liu et al study cellulose and lignin flour. They separated cellulose and lignin flour from wood flour and added with polypropylene (PP) and poly (lactic

acid) (PLA) to make composites. They observed that cellulose flour benefited to most mechanical properties of the composites, while lignin flour reduced water uptake and improved thermal stability [42].

## **1.2. Polymer Nanocomposites**

Polymer nanocomposites define as a composite system containing a polymer matrix and homogeneously dispersed particles having at least one dimension below 100 nm. The excellent properties of nanocomposites attribute to the large surface to volume ratio of the nano fillers [44]. In the early 90s, Toyota research group synthesized nanoclay (layered-silicate) based nylon-6 nanocomposites that exhibited significant improvement in mechanical properties and heat deflection temperature [45]. Latter on these materials commercialized and they used in Toyota cars. After this discovery, the number of papers published about nanocomposites [46].

### **1.2.1. Carbon nanomaterials**

Among the nanoscale carbon based materials, carbon allotropes such as fullerene, single/multi wall carbon nanotubes (CNTs), graphite, diamond and graphene have gained significant importance because of their excellent properties and wide range of application area [47].

Within the nanoscale materials, carbon nanotubes and graphene are more attractive for a variety of applications. Furthermore, carbon nanotubes and graphene have gained significant attention since their discovery in 1991 and 2004, respectively. These new class of materials have large application area. Examples of some potential application areas are actuators, solar cells, field emission device, field effect transistor, supercapacitors and batteries [48]. Moreover, CNT and graphene are known as one and two-dimensional nanostructures, respectively. These structures are mutually complementary in both structure and properties and have beneficial properties, such as ultra-high mechanical strength and electrical conductivity.

Pingan Song et al. [49] reported an eco-friendly technique for manufacturing the polymer nanocomposites. In this work, graphene sheets were dispersed in the polymer matrix via melt-blending technique. The graphene coated by PP latex then melts blending the coated graphene with PP matrix. In this work, mechanical properties of PP were improved by adding of only 0.42 vol % of graphene.

Yield strength of PP was increased nearly 75% and young's modulus of PP was increased nearly 74%. Hailong Fan et al. [50] graphene/chitosan films fabricated with solution casting method. Composite films containing chitosan and graphene analyzed in terms of their mechanical properties in this work. To conclude, the results showed a 200% increase in the elastic modulus of composite containing small amount of graphene compared to that of composite containing only chitosan. Another study, graphene–polyvinylidene fluoride nanocomposite films synthesized and used of this nanocomposite as strain sensor [51].

### **1.2.2. Nanoclay-based polymer nanocomposites**

After the discovery of nanoclay (layered-silicate) based nylon-6 nanocomposites, the number of published papers about the nanocomposites has increased enormously. Liu et al. [52] reported that mechanical properties of composite used in this work were improved with addition of clay. Compared to the neat polymer, storage elastic modulus of clay reinforced composite was higher than 100%. Usuki et al. [13] studied with composite containing only 4.2wt % clay. The strength, tensile modulus, and impact resistance of composite was increased respectively, 50%, 100%, and 20% with addition of small amount of clay in this study. Li et al. [53] manufactured clay based nanocomposite by using electrospinning technique and aqueous formic acid as the solvent. The addition of clay layer increased the solution viscosity significantly and changed morphology of composite. In another study, Jawahar and Balasubramanian manufactured the glass fiber reinforced polyester composite and hybrid nanoclay-fiber reinforced composites [54]. In this study, the composites were prepared with a glass fiber consist of 25 vol % glass fiber and consist of nanosize clay platelets was varied from 0.5-2.5 vol %. The results showed that the hybrid clay-fiber reinforced polyester composite have better tensile, flexural, impact, and barrier properties, storage modulus, and glass transition temperature.

### **1.2.3. Nanocellulose-based polymer nanocomposites**

Cellulose is a polymer, which can be found in the nature abundantly, and it can be obtained from many various plants and living organisms. Moreover, cellulose fibers can use as a reinforcing material due to the many advantages such as abundantly available, low weight, biodegradable, cheaper, renewable, low abrasive nature, and exhibiting good mechanical properties [55]. In recent years, scientists have

succeed in producing cellulose in different morphologies such as whiskers and fibrils, which can reinforce the polymer matrices enormously. Over the last few years the use of cellulosic materials in composite industry has increased due to their relative cheapness compared to the conventional reinforcement materials [56].

Johan M. Felix and Paul Gatenholm [43] studied the cellulose - polypropylene-maleic anhydride copolymer. It was shown that cellulose can reinforce copolymer matrix. In this study loading of cellulose, fibers changed the physical and the chemical properties of composites. These changes were investigated by contact angle measurements and FTIR technique. In another study, polyvinyl alcohol (PVA)/starch blend films were prepared by Lani et al. [57]. In this work, PVA/starch films were reinforced with different content of nanocellulose by solution casting method. Compared to unreinforced film, addition of cellulose fibers significantly improved properties of (PVA)/starch blend films.

The strength and elongation at break improved with addition of 5 % (v/v) of nanocellulose. Moreover, (PVA)/starch blend films have good water resistance and biodegradability. Nakagaito et al. [58], Suryanegara et al. [59] and Iwatake et al. [60] studied microfibrillated cellulose (MFC)-PLA nanocomposites. It was shown that MFC can reinforce PLA 40% [19] and MFC acts as nucleating agent and increases the crystallinity, accompanied with a tensile modulus increase of 42% [60].

### **1.3. Natural Fiber Composites for Automotive Applications**

The materials used in automotive industry need to satisfy several criteria. These are lightweight, safety, crash worthiness, cost, recycling and life cycle. Some of the criteria are regulated due to environmental concerns and some are the requirements of the customer's needs [61]. As a result, manufacturers and engineers always aim at developing of new materials and improving processes to use in manufacturing better products. Thus they increase their profit margin in these ways [9].

In this regard, the lightweight, low cost natural fibers offer the possibility to manufacturing ecofriendly products in several automotive interior and exterior parts. Natural fiber composites (NFCs) are the most dynamic sectors of today's plastic industry with an average annual growth rate of approximately 18% in Northern America and 14% in Europe [62]. They have a large applications area in automotive industry and they are used for different applications such as boot linens, parcel

shelves, seat backs, sunroof sliders, front door linens, rear door linens, and headliners [9, 10]. On the other hand, they are providing some important benefits such as recyclability, biodegradability, and abundantly availability [61]. The usage of natural fibers such as kenaf, sisal, flax, jute, and hemp in the automobile components reduces the automobile weight, CO<sub>2</sub> release, and fuel consumption.

Automotive components including natural fiber is currently being used by many vehicle manufacturers such as Audi, Opel, Daimler-Chrysler, Fiat, Ford, Mercedes Benz, Peugeot, Renault, Volvo, VW, Volkswagen and BMW [9]. Manufacturers of Mercedes used the jute reinforced epoxy matrix composites as door panels in their vehicles back in 1996. Then, polyester/flax-reinforced composite material used in order to increase sound insulation of vehicle in Mercedes-Benz Travego travel coach model in 2002. Some years later, Daimler Chrysler AG (Stuttgart, Germany) started using fiber reinforced composite materials. Daimler Chrysler AG (Stuttgart, Germany) used abaca plant instead of fiberglass for the production of the spare tire well covers of the Mercedes-Benz A-Class, two-door coupe vehicle in 2004 [63]. Two special polyamides belonging to the BASF Ultramid® family and Napoleon® expanded PP foam are used in new Opel Insignia OPC as a front seat. Opel and Recaro develop this product [64]. Audi used polyurethane reinforced with a mixed flax/sisal material as door trim panels in 2000 [9]. BMW Group incorporates a considerable amount of renewable raw materials in its vehicles, including 10,000 tonnes of natural fibers in 2004 [65]. In another study, PP wood flour composites used as door panel in Fiat Punto, Bravo, Alfa vehicles model [10].

#### **1.4. Objective**

The objective of this study is to manufacture of nanocellulose–polypropylene composites with and without coupling agents and discusses their possible application areas in automotive industry.

## **2. EXPERIMENTAL PROCEDURE**

### **2.1. Materials**

Polypropylene, Impact Copolymer Moplen2000HEXP (Melt flow rate: 16 g/10 min. (230 °C/2.16 kg), density: 0.9 g/cm<sup>3</sup>) was provided by Lyondell Basell Polymers. Cellulose nanofibers (CNF) with diameter of 0.02 microns, was provided as slurries of approximately 4% solids by Process Development Center in The University of Maine.

Maleic anhydride grafted polypropylene (MAPP); OREVAC® CA 100 was purchased from Arkema Inc. (Philadelphia, PA, USA). OREVAC® CA 100 is a chemically functionalized polypropylene with a high content of maleic anhydride. It is melt flow index is 10 g/10 min.

Fusabond (Fusabond® E265) was purchased from DuPont Packaging & Industrial Polymers. DuPont™ Fusabond® E265 is an anhydride modified high-density polyethylene. It is melt flow rate (190 °C/2.16kg):12 g/10 min.

### **2.2. Materials Processing**

LabTech Twin-Screw Extruder (screw diameter: 20mm, L/D ratio of 32:1) was used to produce nanocellulose–polypropylene (NC/PP) composites. First, nanocellulose was oven-dried at 35-37 °C for 24 hours. Second, it was put into laboratory mixer for 8 minutes to minimize the water content. Then, NC/PP composite containing 2wt % nanocellulose was manufactured. In this process, the extrusion temperature profile was 190 °C, 200 °C, 210 °C, 210 °C, 210 °C, and 220 °C from the feeding zone to the die and the extruder rotation speed was 190 rpm. Furthermore, NC/PP composite containing 2wt % nanocellulose treated with Fusabond and treated with MAPP. In this treatment three different percentage were studied (0.1wt %, 0.5 w t%, 1wt %) for Fusabond and were studied (1wt %, 2 w t%, 3wt %) for MAPP. NC/PP composites with and without coupling agents were manufactured based on 1kg. The amounts of materials are shown in Table 2.1.

**Table 2. 1:** The amount of materials

<b>Composite Sample</b>	<b>Amount of PP</b>	<b>Amount of Nanocellulose</b>	<b>Amount of Coupling agent</b>
Untreated NC/PP composite	980 gr	20 gr	-
NC/PP composite treated with 1wt % MAPP	970 gr	20 gr	10 gr
NC/PP composite treated with 2wt % MAPP	960 gr	20 gr	20 gr
NC/PP composite treated with 3wt % MAPP	950 gr	20 gr	30 gr
NC/PP composite treated with 0.1wt% Fusabond	979 gr	20 gr	1 gr
NC/PP composite treated with 0.5wt% Fusabond	975 gr	20 gr	5 gr
NC/PP composite treated with 1wt% Fusabond	970 gr	20 gr	10gr

The extruded composites were pelletized and they were dried at room temperature for a week. Then, these composite pellets were pressed by LabTech hydraulic hot press under the pressure of 39 bar to manufacture of composite plates. In this process, upper and lower heaters were 200 °C. Pellets heated for 20 second in a hot chamber and cooled for 2 minutes in a cold chamber. Moreover, composite pellets were mixed by gelimat mixer for 15 second prior to pressing. Finally, the samples prepared in this study are coded and they are shown in Table 2.2.

**Table 2. 2:** The code of samples

<b>Samples</b>	<b>Sample Codes</b>
PP	E0
Untreated NC/PP composite	E1
NC/PP composite treated with 1wt % MAPP	E2
NC/PP composite treated with 2wt % MAPP	E3
NC/PP composite treated with 3wt % MAPP	E4
NC/PP composite treated with 0.1wt% Fusabond	E5
NC/PP composite treated with 0.5wt% Fusabond	E6
NC/PP composite treated with 1wt% Fusabond	E7



## **2.3. Characterization**

### **2.3.1. Microscopy**

The morphology of neat PP and composites were investigated via scanning electron microscopy. SEM images were taken from the fracture surfaces of the tensile specimens. VEGA3 TC TESCAN was used as SEM. The samples were coated with gold and the images and accelerated voltage was adjusted as 30 kV and images were taken at different magnifications.

### **2.3.2. Mechanical testing**

The mechanical properties such as the tensile strength, the value of elongation at break, and the value of Young's Modulus of composite samples and neat PP were characterized by tensile testing. The test samples were prepared according to the ASTM D638 standard. Then, the mechanical properties of samples were tested by SHIMADZU AGS-X tensile testing machine with a 5kN load cell and testing speed of 50mm/min.

### **2.3.3. Fourier Transform Infrared Spectroscopy (FTIR)**

The FTIR technique was used to study the main functional groups present in materials used in this study. Thermo Scientific TM FTIR spectrometer in Attenuated total reflection infrared (ATR-IR) mode was used to obtain the spectra of samples. Attenuated total reflection infrared (ATR-IR) spectra of the materials were collected at a resolution of  $4\text{ cm}^{-1}$  and a number of 16 scans per sample. Spectral outputs were recorded in absorbance mode as a function of wave number.

### **2.3.4. Thermo Gravimetric Analysis (TGA)**

The thermal stability of composite samples and neat PP were studied by thermogravimetric analysis technique. Thermal properties of composite samples and neat PP were analyzed by Simultaneous Thermal Analyzer (STA) 8000 machine. The samples were heated from  $10\text{ }^{\circ}\text{C}$  to  $700\text{ }^{\circ}\text{C}$  for at a heating rate of  $10\text{ }^{\circ}\text{C}/\text{min}$ . under nitrogen flow.

### **2.3.5. Dynamic Mechanical Analysis (DMA)**

Dynamic mechanical analysis gives information about the modulus values with respect to changes in the temperature during testing. TA Instrument Q800 machine was used to determine the modulus value of composite samples and neat PP. The tested materials have dimensions of 17.5×12.2×2.3 mm. Moreover, the tested materials were heated from 30 °C to 120 °C with a heating rate 3 °C/min. The applied frequency was 1 Hz.

### **2.3.6. Contact angle measurements**

The hydrophobicity of composite samples were studied with contact angle measurements, using a KSV Attension Theta Lite Optical Tensiometer, combined with a high-speed camera. Water droplets were deposited directly at the top surfaces of the material, and the water contact angles were measured.

### 3. RESULT AND DISCUSSIONS

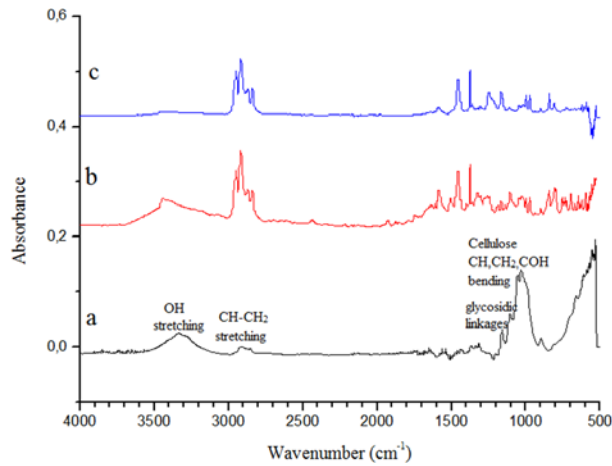
#### 3.1. Fourier Transform Infrared Spectroscopy (FTIR) Measurements Results

The FTIR technique was used to study the main functional groups present in cellulosic fibers composites with and without coupling agents. The most distinct spectral peaks published about cellulosic fibers (Table 3.1). Chanel stated that the bands assigned in O-H stretch at  $3300\text{ cm}^{-1}$ , the C-H asymmetric stretch at  $2900\text{ cm}^{-1}$ , the C-H symmetric stretch at  $2850\text{ cm}^{-1}$ , the C=O stretch of a carboxylic acid and ester at  $1700\text{ cm}^{-1}$ , and the C=O stretch of an acid salt at  $1600\text{ cm}^{-1}$  [66]. Rosli et al. the spectra of cellulosic fibers exhibited C=O stretching vibration at  $1735\text{ cm}^{-1}$ , O-H stretching vibration at  $3400\text{-}3300\text{ cm}^{-1}$ , O-H bending of absorbed water at  $1627\text{-}1638\text{ cm}^{-1}$  [67]. Zain et al. observed the spectra of cellulosic fibers and reported that the typical absorption band that appears in the extracted cellulose and nanocellulose from pomelo albedo spectra is similar to the characteristic of pure cellulose extracted from orange peel at  $3426, 1631, 1434, 1031$  and  $895\text{ cm}^{-1}$  [68]. Ioan Bicu and Fanica Mustata extracted the cellulose from orange peel and observed the characteristic peaks of cellulose [69].

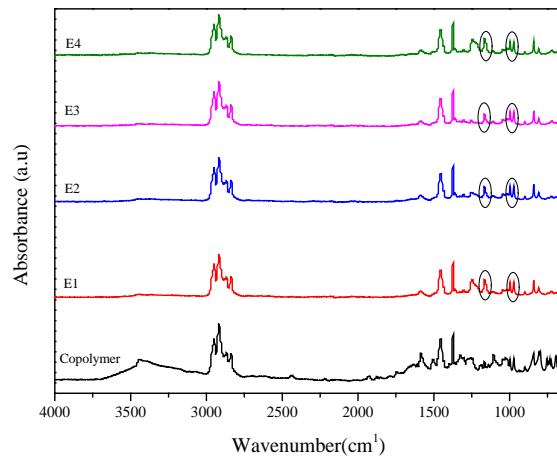
**Table 3. 1:** Infrared band assignments for the cellulosic fibers

Position / $\text{cm}^{-1}$	Assignment	References
~ 3335	Intra-molecular OH stretching vibration	[66, 67, 70]
~ 2900	C-H asymmetrically stretching vibration	[66-68]
~ 1635	Adsorbed water and oxygen-containing group	[67-70]
~ 1735	stretching vibration of C=O	[66-68, 70]
~1060	C-O,C-H stretching vibrations of Cellulose	[68, 70]
~1163	Cellulose and hemicellulose C-O-C stretching vibration	[70, 72]
~1372	Cellulose and hemicellulose C-H bending vibration	[69, 72]
~2899	Cellulose CH stretching vibration	[69, 72]
~1315	CH in plane deformation of CH <sub>2</sub> groups	[73, 74]
~898	Correspond to $\beta$ -1, 4 glycosidic linkages	[73, 74]

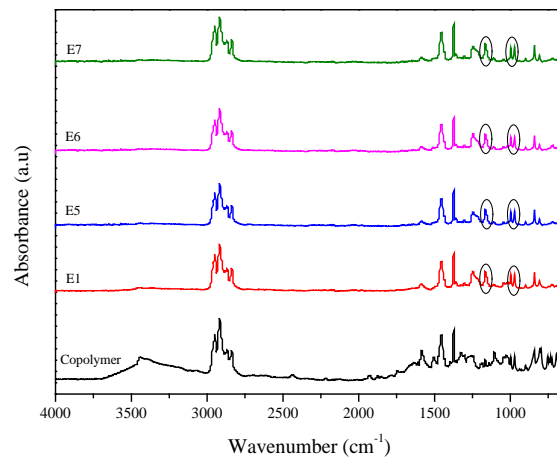
The FTIR spectroscopic analysis of neat PP and NC/PP composites are shown in Figure 3.1-3.3. The FTIR spectra of the PP and NC/PP composite containing 2wt % NC are shown in Figure 3.1.



**Figure 3. 1:** FTIR spectra of a) neat NC b) neat PP c) untreated NC/PP composite



**Figure 3. 2:** FTIR spectra of PP, untreated and MAPP treated NC/PP composites



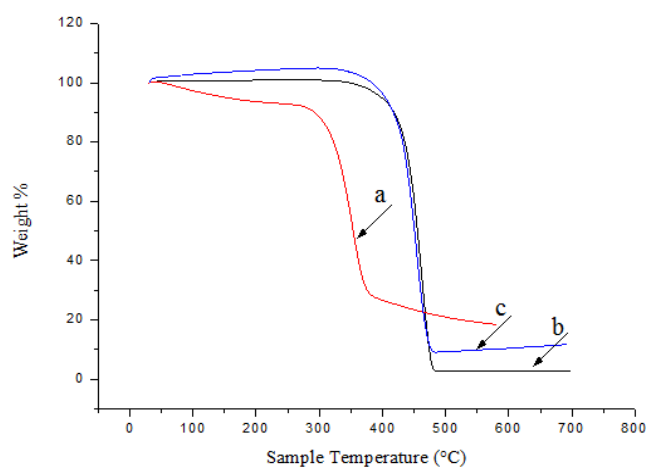
**Figure 3. 3:** FTIR spectra of PP, untreated and FUSE treated NC/PP composites

One of the peaks at  $3335\text{ cm}^{-1}$  disappeared in the PP structure after 2wt % nanocellulose addition (Figure 3.1). Zain et al. [68] stated that there is O-H stretching vibration and O-H bending of the absorbed water, respectively. This was attributed to

cellulose are inter molecularly bonded to PP chain. On the other hand, the peak at around  $1057\text{ cm}^{-1}$  and  $1060\text{ cm}^{-1}$  were observed with addition of 2wt % nanocellulose. The band around  $1057\text{ cm}^{-1}$  corresponds to C-O-C skeletal vibration and the band around  $1060\text{ cm}^{-1}$  that represents C-O and C-H stretching vibration, confirms the structure of cellulose. Furthermore, increase the intensity of these groups indicates to the increase of crystallinity of the samples [70]. In this study, composite samples exhibited the nearly same absorbance band intensity around  $1060\text{ cm}^{-1}$  and indicated the nearly same crystallinity (Figure 3.2 and 3.3). Another band observed around  $898\text{ cm}^{-1}$ . This peak is the most significant absorbance band, which corresponds to glycosidic -C-H deformation, with a ring vibration contribution on -O-H bending [71]. These features are characteristic linkage between the anhydroglucose units in cellulose [68]. Typical absorbance bands of cellulose at  $1428$ ,  $1368$ ,  $1315$ ,  $1261.4$ ,  $1054$ , and  $898\text{ cm}^{-1}$  were observed in all NC/PP composites but the characteristic peaks intensities of cellulose increased in the Fusabond treatment compared to that of MAPP treatment. In this regard, we can say that addition of Fusabond increased the interfacial adhesion between the PP and NC [71].

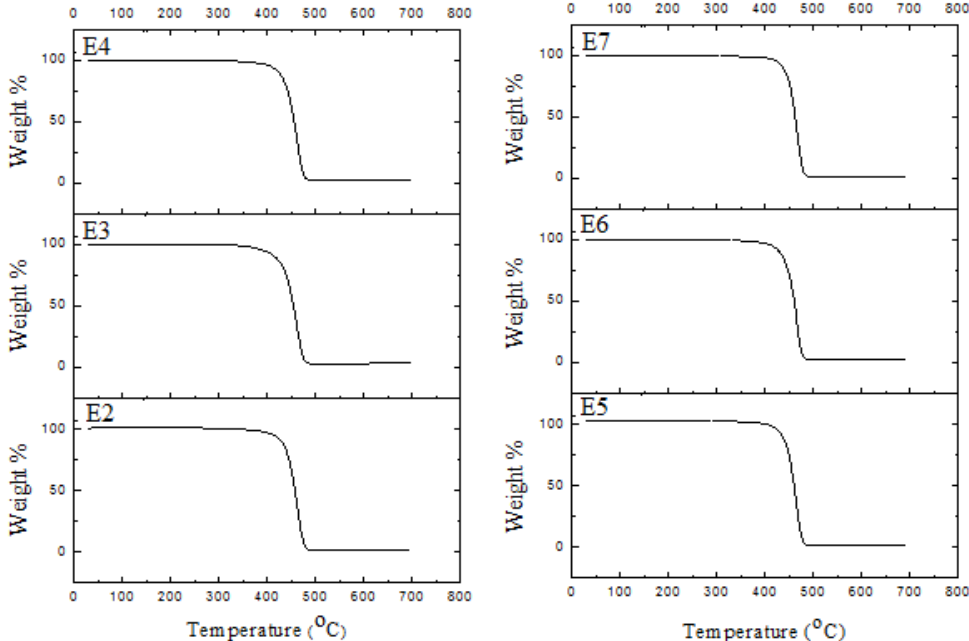
### 3.2. Thermo Gravimetric Analysis (TGA) Results

Thermogravimetric analysis was conducted a nitrogen atmosphere to investigate the thermal stability of composite materials. Nanocellulose and nanocellulose-polypropylene composites exhibits single degradation step are shown in (Figure 3.4 and Figure 3.5).



**Figure 3. 4:** TGA curves of a) neat NC b) neat PP c) untreated NC/PP composite

This was determined from weight changes in TGA curves. Compare to the NC/PP composites, small weight loss occurred in pure cellulose between 50-150 °C that is attributed to the removal of absorbed water in cellulose [75, 76]. Then pure nanocellulose sample indicated a more pronounced degradation process at around 280 °C to 370 °C. This is the consistent with data obtained by Poletto et al. [77]. Moreover, the TGA of neat PP showed a single degradation step, starting at 348 °C. This is the consistent with data obtained by Rafel et al [78]. The TGA of treated composites also followed the similar degradation patterns.



**Figure 3.5:** TGA curves of MAPP treated samples and Fusabond treated samples

Thermogram of composite treated with 0.1wt % Fusabond exhibits single stage decomposition starting from 402 to 485 °C (Figure 3.5). The region between 200-400 °C in composite treated with 0.1wt % Fosabond is almost linear and accounts for meager 3% weight loss due to moisture. Rate of decomposition is very fast between the region 430-485 °C resulting in 91% weight loss. It can be ascribed to dehydration, depolymerization and pyrolysis at higher temperature. It stabilizes and tremendously slows down in the temperature range 300-410 °C, accounting for only 5% weight loss. The final degradation temperature is recorded at 485 °C leaving behind 1% residue. In case of composite treated with 0.5wt % Fusabond initial decomposition temperature is observed at 330 °C and degradation completes at 485 °C leaving 2% residue. Decomposition curve shows that degradation completes at 390-500 °C region, resulting 96% weight loss. Furthermore, composite treated with 1wt % Fusabond exhibits single stage decomposition starting from 300 to 487 °C.

This degradation indicated the pyrolysis of cellulose and PP because it was mainly happened at 315– 400 °C [79, 80]. Rate of decomposition is very fast between the region 380 – 487 °C resulting in 97% weight loss. The final degradation temperature was recorded at 487 °C leaving behind 1% residue.

Thermogram of composite treated with MAPP exhibits single stage decomposition as in other composite samples. It was shown in Figure 3.5. In case of composite treated with 1wt % MAPP initial decomposition temperature is observed at 340 °C and degradation completes at 485 °C leaving 2% residue. Moreover, initial decomposition temperature of treated composites (treated with 2wt % MAPP and treated with 3wt % MAPP) were observed at around the 300 °C. Dehydration, depolymerization, and pyrolysis were occurred in the region between 330-480 °C in composite treated with 2wt % MAPP and it was occurred in the region between 350-500 °C in composite treated with 3wt % MAPP.

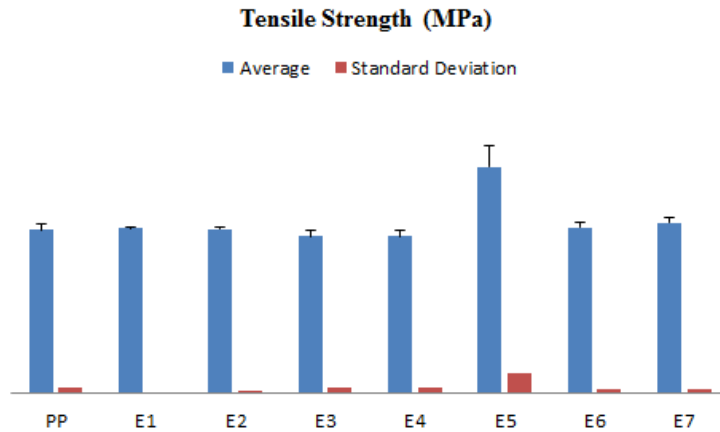
On the other hand, onset temperature of neat PP slightly decreased with addition of 2wt % nanocellulose because cellulose has the hydrophilic nature. However, onset temperature and thermal stability of NC/PP composite slightly increased with addition of Fusabond. The TGA analysis results show that the thermal stability of NC/PP composites did not change much but addition of Fusabond was improved the composite thermal stability and homogeneity (Table 3.2).

**Table 3. 2:** Onset temperature of neat PP and NC/PP composites

<b>Sample Code</b>	<b>T<sub>onset</sub>(°C)</b>
E0	443.1
E1	424.16
E2	439.08
E3	436.12
E4	434.86
E5	440.18
E6	442.20
E7	447.27

### 3.3. Mechanical Testing Results

The reinforcement effect of coupling agent on the mechanical properties of nanocellulose–polypropylene composites was evaluated as a function of the coupling agent content. The tensile strength, elongation at break, and the Young’s Modulus of NC/PP nanocomposites were characterized by tensile testing. These properties are shown in Figure 3.6-8.



**Figure 3.6:** Tensile strength of neat PP, untreated NC/PP composite, and treated NC/PP composites

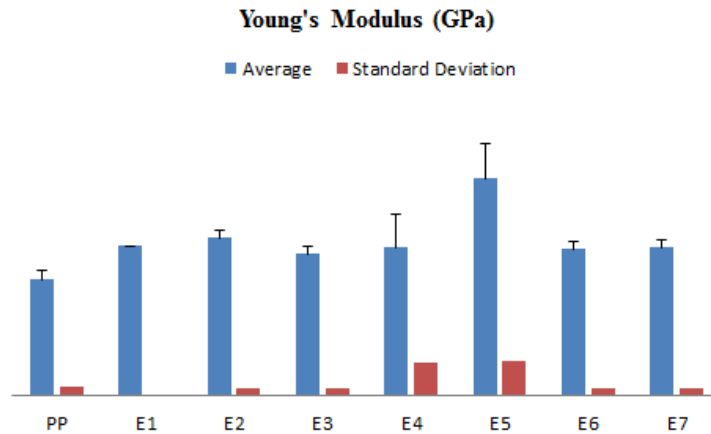
In the samples E2, E3 and E4 was studied MAPP coupling agent with different percentages (1wt %, 2wt %, 3wt %) while E5, E6, and E7 was studied Fusabond coupling agent (0.1wt %, 0.5wt %, 1wt %). The results show that the loading of Fusabond with 0.1wt % increased the strength of composite.

Composite samples except for containing 0.1wt % Fusabond exhibited the very similar result in terms of tensile strength. Compared to the pure PP, the tensile strength of sample containing 0.1wt % Fusabond was higher than 38%. The interfacial interaction of the nanocellulose and the polypropylene was very important in order to increase the mechanical properties.

This result consistent with the FTIR spectroscopy because, characteristic peaks intensities of cellulose increased in the Fusabond treatment. When the MAPP treated samples, tensile strength of nanocomposite did not qualitatively change. This is consistent with the data obtained by Pérez et al. [81].

They studied with PP/wood flour composites. In this study, the effect of composition and the incorporation of MAPP on the materials tensile, fracture and failure behavior was investigated. The incorporation of MAPP in the composites formulation did not qualitatively change the materials tensile behavior.

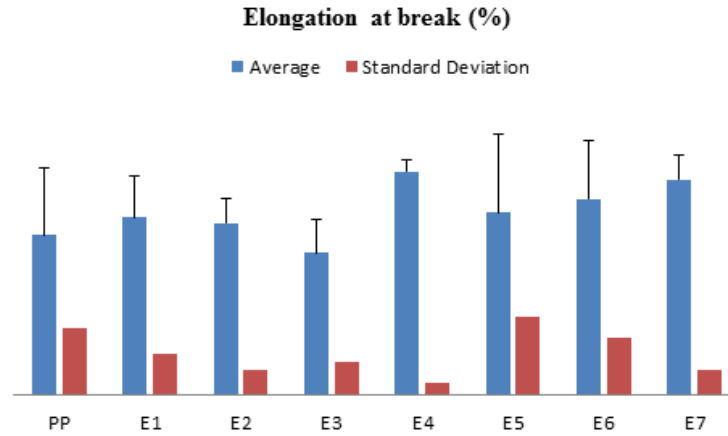




**Figure 3.7:** Young's Modulus of neat PP, untreated NC/PP composite, and treated NC/PP composites

Young's (elastic) Modulus may be thought of as stiffness, or material's resistance to elastic deformation [82]. The greater the modulus, the stiffer, or smaller the elastic strain that result from the application of a given stress. Compared to the pure PP, stiffness of composite samples exhibited improvement. The stiffness values for composites, in the range from 0.736 GPa to 1.067 GPa against the value of 0.57 GPa for pure polypropylene. Generally, the stiffness is directly related to the porosity content of composites [82]. The sample E2 exhibited the better result than other MAPP treated samples but all samples treated with MAPP exhibited the very close stiffness value.

This is consistent with the data obtained by Dányádi L. et al. [83]. They have observed also very close mechanical properties for MAPP treated wood flour composites. Furthermore, sample treated with 2wt % MAPP exhibited the worst stiffness value than other composite samples. This sample exhibited the worst stiffness value because it has the worst morphology. Moreover, the stiffness of the 0.1wt % Fusabond exhibited better stiffness than other samples. Thus, we conclude that this sample has the smallest porosity content. Compared to the pure PP, the Young's (elastic) Modulus of the 0.1wt % Fusabond containing PP nanocomposites was higher than 87%. The elongation at break values of the composites line diagram plotted against coupling agent content between E2 and E7 in Figure 3.8. The MAPP treated sample E3 that consist of 2wt % MAPP content indicated the worst elongation at break while E4 that consist of 3wt % MAPP exhibited the best elongation value at break.



**Figure 3.8:** Elongation at break of neat PP, untreated NC/PP composite, and treated NC/PP composites

Moreover, elongation at break slightly increased while increasing weight percentage of Fusabond from 0.1wt % to 1wt %. In almost all composites, the interface between fibres and matrix is of importance for the mechanical properties as well as for other characteristics related to the performance of the materials and components. Some important mechanical properties are shown in the Table 3.3.

**Table 3.3:** Mechanical properties of neat PP and NC/PP composites

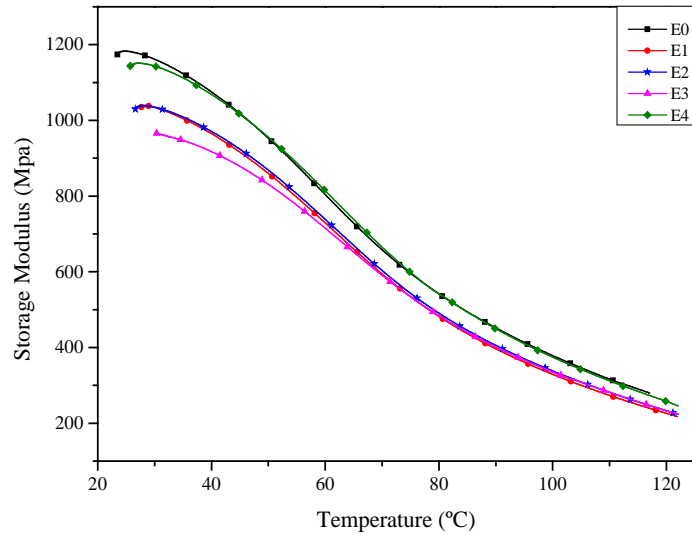
Sample	Tensile Strength (MPa)	Young's Modulus (GPa)	Elongation at break (%)
E0	14.45 ± 0.5	0.570 ± 0.047	14 ± 5.9
E1	14.56 ± 0.15	0.736 ± 0.055	15.56 ± 3.6
E2	14.50 ± 0.17	0.775 ± 0.04	15.05 ± 2.2
E3	13.86 ± 0.49	0.697 ± 0.035	12.47 ± 2.9
E4	13.84 ± 0.49	0.729 ± 0.165	19.55 ± 1.05
E5	19.99 ± 1.8	1.067 ± 0.173	15.99 ± 6.8
E6	14.62 ± 0.43	0.720 ± 0.038	17.17 ± 5.05
E7	15.09 ± 0.39	0.730 ± 0.033	18.85 ± 2.2

In the present study, small amount of nanocellulose (2wt %) was loaded polypropylene matrix polymer without coupling agents to perform the effect of this small loading. Then, coupling agents were loaded to improve the mechanical properties and interfacial adhesion of polypropylene and nanocellulose. The results showed a 38% increase in the tensile strength and showed an 87% increase in the Young's Modulus of NC/PP composite containing 0.1wt % Fusabond compared to that of neat polypropylene. This is consistent with the data obtained by Krishnan et

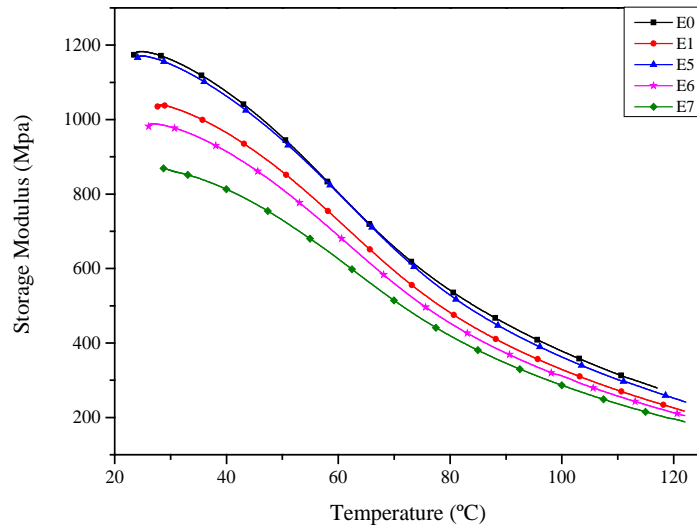
al. [84] and Hietala et al. [82]. According to their results, mechanical properties improved with effectively loading of cellulose fibers.

### 3.4. Dynamic Mechanical Analysis (DMA) Results

The DMA results of pure polypropylene, nanocellulose and polypropylene-nanocellulose composites are shown in Figure 3.9 and Figure 3.10.



**Figure 3.9:** DMA curves of PP, NC and MAPP treated samples



**Figure 3.10:** DMA curves of PP, NC and FUSE treated samples

Dynamic mechanical analysis gives information about the modulus values with respect to changes in the temperature during testing. NC/PP composites were tested in a temperature scale between the 30 °C-120 °C. The modulus value of neat PP decreased at all temperatures compared to that of composite samples. However, the modulus values of the composite containing 0.1wt % Fusabond exhibited the better

results than other composite samples. This result is consistent with the tensile testing results. Moreover, the homogeneity of Fusabond treated samples decrease with increasing amount of Fusabond content in the range of 0.1-1wt %. This result is consistent with contact angle measurements because increasing amount of Fusabond decreased samples hydrophobicity and homogeneity. Therefore, the values of storage modulus decreased with increasing amount of Fusabond content (Table 3.4).

**Table 3.4:** Storage modulus (MPa) of neat PP and NC/PP composites

Sample	30 (°C)	60 (°C)	90 (°C)	120 (°C)
E0	1156.64	789.86	444.18	275.52
E1	1033.56	727.79	395.62	225.23
E2	1034.70	737.54	404.69	232.37
E3	966.23	714.91	401.11	232.79
E4	1143.00	812.03	448.26	256.65
E5	1148.07	801.44	435.19	251.89
E6	979.64	686.62	372.91	212.91
E7	863.33	625.53	345.55	196.14

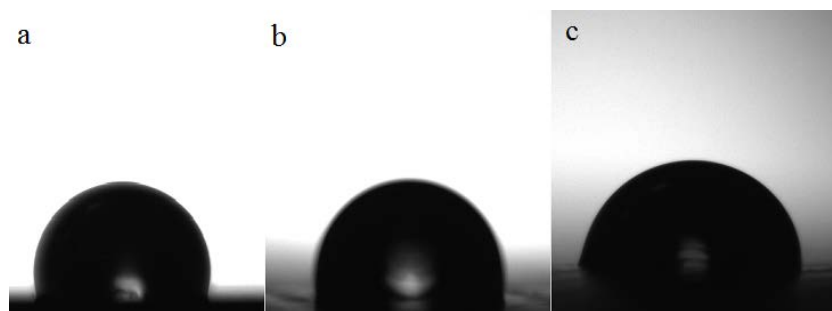
### 3.5. Contact Angle Measurements Results

Wettability studies usually involve the measurement of contact angles as the primary data, which indicates the degree of wetting when a solid and liquid interact. A contact angle less than 90° (low contact angle) correspond to high wettability, while large contact angles greater than 90° (high contact angle) correspond to low wettability [85]. The interaction of the NC/PP composites structure with water was investigated by contact angle, and the data are shown in Table 3.5. Wettability is an important property to adhesion of cellulosic materials [86]. Wetting quality of this types of materials are influenced by many factors including macroscopic characteristics, surface quality, processing temperature, and properties of adhesives (e.g., acidity, rheology, and viscosity) [87-89]. Therefore, the wettability of composites were studied by contact angle measurements and results of measurements are shown in Table 3.5.

**Table 3.5:** Contact angle measurement results

Sample	CA left [°]	CA right [°]	CA mean [°]
E0	80.21	82.36	81.28
E1	121.92	121.90	121.91
E2	116.72	118.70	117.71
E3	89.94	95.86	92.90
E4	105.11	105.03	105.07
E5	112.15	112.15	112.15
E6	99.92	99.90	99.91
E7	98.20	95.94	97.07

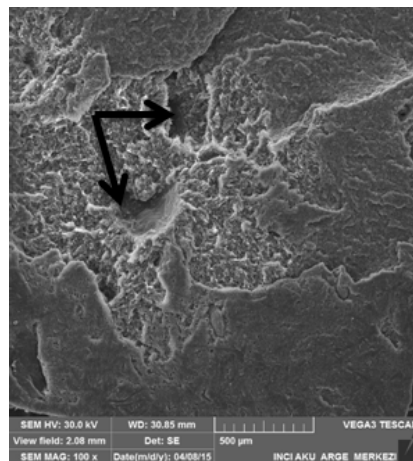
More specifically, a contact angle less than 90° indicates that wetting of the surface is favorable, and the fluid will spread over a large area on the surface; while contact angles greater than 90° generally means that wetting of the surface is unfavorable so the fluid will minimize its contact with the surface and form a compact liquid droplet [85]. In the first, composite containing 2wt % nanocellulose treated with MAPP (Figure 3.12). In this treatment, composite containig 1wt % MAPP show the highest hydrophobicity (CA value: 117°) while composite containig 2wt % MAPP (CA value: 92°) show the lowest hydrophobicity and composite treated with 3wt % MAPP indicated CA value is 105°.



**Figure 3.11:** Contact angle images of a) NC/PP composite treated with 1wt % MAPP b) NC/PP composite treated with 3wt % MAPP c) NC/PP composite treated with 2wt % MAPP

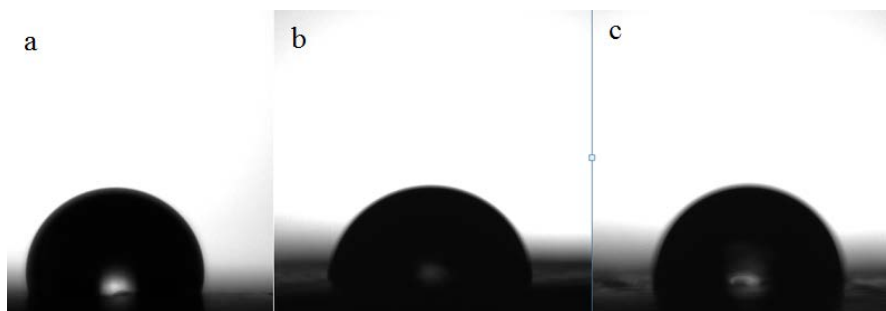
In the some works were reported for MAPP treatments. Matuana et al. [90] were studied four different coupling agents to treat wood veneer and investigated the wettability of treated wood specimens. For specimens treated with anhydride-based coupling agents contact angles results were reported the range from 100° to 110°. This is consistent with the data obtained by Lu et al. [91]. According to these studies,

MAPP treated samples indicated the contact angles value the range from 100° to 130°. These data consistent with our results except for 2wt % MAPP treated composite. Composite containing 2wt % MAPP indicated the lowest hydrophobicity because wetting quality of materials depend on many factors including porosity, surface roughness, wood surface polarity and moisture content. Morphology of this sample is shown in Figure 3.13. In the microscope image of composite containing 2wt % MAPP, some holes exist on the surface and this inhomogeneous surface caused the decreasing of CA value.



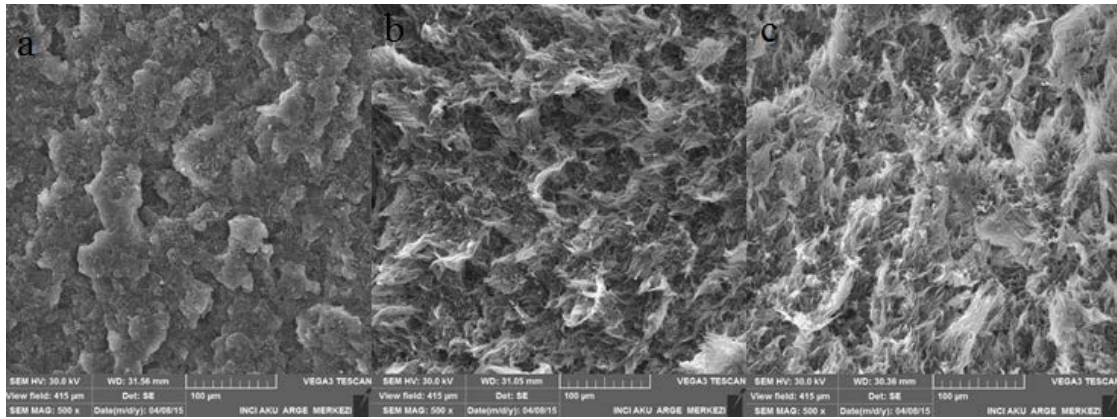
**Figure 3.12:** SEM images of NC/PP composite treated with 2wt % MAPP

In the second, composite containing 2wt % nanocellulose treated with Fusabond (Figure 3.14). In this treatment, composite treated with 0.1wt % Fusabond indicated the highest CA value was 112°.



**Figure 3.13:** Contact angle images of a) NC/PP composite treated with 0.1wt % Fusabond b) NC/PP composite treated with 0.5wt %Fusabond c) NC/PP composite treated with 1wt % Fusabond

Furthermore, CA values and homogeneity of composites treated with Fusabond decreased with increasing amount of Fusabond. They are shown in Figure 3.15 and Table 3.5.

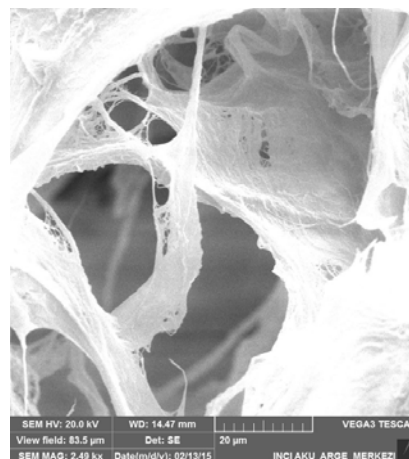


**Figure 3.14:** SEM images of a) NC/PP composite treated with 0.1wt % Fusabond b) NC/PP composite treated with 0.5wt % Fusabond c) NC/PP composite treated with 1wt % Fusabond

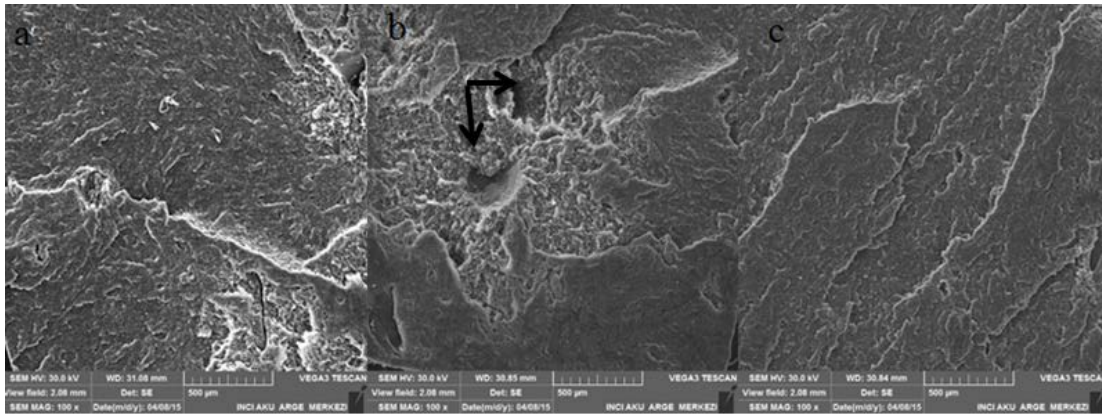
Cellulose fibers became observable and the homogeneity of the composite decreased in the case of increasing Fusabond content. The existence of cellulose fibers on the composite surface led to decrease CA value, because cellulose has the hydrophilic nature. Therefore, CA value of Fusabond treated composites decreased while increasing amount of Fusabond.

### 3.6. Microscopic Analysis

In the Figures 3.16-3.18, three different structures are shown. Figure 3.16 show the neat nanocellulose structure and it is possible to see the cellulose fibrils in this image. Figures 3.17 and 3.18 show the morphology of composites treated with coupling agents.



**Figure 3.15:** SEM images of neat NC

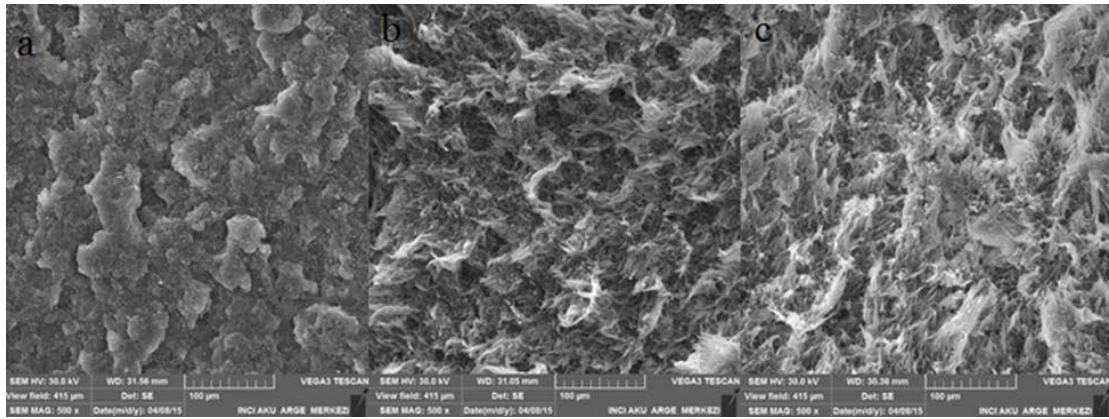


**Figure 3.16:** SEM images of a) NC/PP composite treated with 1wt % MAPP b) NC/PP composite treated with 2wt % MAPP c) NC/PP composite treated with 3wt % MAPP

SEM images of fracture surfaces of MAPP treated composite samples are shown in Figure 3.17. Figure 3.17 (b) indicates the morphology of composite treated with 2wt % MAPP and the morphology of this sample clearly show that the interfacial adhesion between the cellulose fiber and polypropylene matrix was poor and some big holes were observed. This is evidence of the poor dispersion between nanocellulose and polypropylene matrix. Compare to the composite treated with 2wt % MAPP, other MAPP treated composite samples exhibited the better morphology. These results was expected because samples treated with 1wt % MAPP and 3wt % MAPP exhibited the better mechanical and thermal properties than sample treated with 2wt % MAPP.

SEM images of fracture surfaces of Fusabond treated composite samples are shown in Figure 3.18. Figure 3.18 (a) indicates the morphology of composite treated with 0.1wt % Fusabond, Figure 3.18 (b) indicates the morphology of composite treated with 0.5wt % Fusabond, and Figure 3.18 (c) indicates the morphology of composite treated with 1wt % Fusabond. SEM images of these composite samples clearly indicate the differences. The composite sample reinforced with 0.1wt % Fusabond exhibited the better dispersion from the other Fusabond treated composites. In this treatment, adhesion between cellulose fibre and polypropylene indicated the better result because cellulose fibers were buried more effectively in the polypropylene matrix from the others sample. On the other hand, the homogeneity of composites treated with Fusabond decreased with increasing amount of Fusabond.





**Figure 3.17:** SEM images of a) NC/PP composite treated with 0.1wt % Fusabond b) NC/PP composite treated with 0.5wt % Fusabond c) NC/PP composite treated with 1wt % Fusabond.



#### 4. CONCLUSIONS

The aim of this study was to prepare nanocellulose–polypropylene composites and discussed their possible application areas in automotive industry. Within the developments in the technology, nanoscale reinforcements have become possible, which have many advantages compared to the micron-sized reinforcements. New types of nanoscale reinforcements have a pioneering role in composite technology and large number of applications in automotive, constructions, marine, electronic, packaging, and aerospace.

This study had three parts. In the first and most comprehensive part, nanocellulose–polypropylene composite containing 2wt % nanocellulose was manufactured. In the second part, nanocellulose–polypropylene composite was reinforced with the two different coupling agents such as MAPP and Fusabond. In the last step, composite materials were characterized in terms of their mechanical, thermal, spectroscopic, and morphological properties.

The most important outcome of this study was to produce nanocomposites of polypropylene with nanocellulose via extrusion technique. In the extrusion technique, optimization of the production conditions of high water content materials is a challenge but the production conditions of nanocellulose–polypropylene composites were optimized carefully in this study. Moreover, the reinforcement effect of coupling agents of nanocomposites was investigated. As compared, the properties of NC/PP composites, nanocomposites treated with Fusabond gave better results.

As a last step in the nanocellulose–polypropylene composites, composite materials were characterized in terms of their mechanical, thermal and spectroscopic properties. Mechanical properties of the composites were analyzed by tensile testing method and dynamic mechanical analysis (DMA) technique. The tensile testing results showed a 38% increase in the tensile strength and showed an 87% increase in the Young's Modulus of NC/PP composite containing 0.1wt % Fusabond compared to that of neat polypropylene. In addition to this, the modulus values of the

nanocomposites containing 0.1wt % Fusabond are higher than the pure polypropylene at temperature 60 °C. The high strength of composite containing 0.1wt % Fusabond was confirmed with the tensile testing as well. On the other hand, interfacial adhesion of polypropylene and cellulose nanofibers (CNF) was characterized by ATR-FTIR spectrum. Composite samples exhibited the nearly same absorbance band intensity in the region of typical absorbance bands of cellulose and indicated the nearly same crystallinity. Furthermore, TGA analysis results show that the thermal stability of NC/PP composites did not change much but slightly increases with addition of coupling agents. This was consistent with FTIR analysis, because crystallinity of samples related to the thermal stability of samples.

To conclude this comprehensive work on nanocellulose–polypropylene composites, it was observed that the best mechanical properties were achieved with addition of 0.1wt % Fusabond. In Table 4.1, the values of tensile strength are given for all composites prepared in this study.

**Table 4.1:** Tensile strength of all composites prepared in this study

Sample	Tensile Strength (MPa)
E0	14.45
E1	14.56
E2	14.50
E3	13.86
E4	13.84
<b>E5</b>	<b>19.99</b>
E6	14.62
E7	15.09

For further work, these findings can be used for automobile part such as cover radiator, dashboards, door panel. The properties availability, renewability, low density and price very important in the automotive applications. The cellulose can be incorporated to thermoplastic to increase the renewability of composites and to decrease the density and price of composites. Moreover, the cellulose can be incorporated to the polypropylene during the synthesis of the polymer, which can be even more effective.

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